Quantum Dot Array Formation through Biomolecular Nanopatterning

Contract No. DAAD19-99-C-0019
Final Report for PHASE I OPTION
18 AUG – 17 DEC 1999

1. 0. INTRODUCTION AND BACKGROUND

The long-term goal of this project is to perfect a technology for creating precisely ordered and precisely located arrays of semiconductor quantum dots. The approach we have adopted is to use biomolecular templates as etch masks, and Low Energy Electron Enhanced Etching (LE4) for pattern transfer, to first create in a substrate an array of holes with diameters comparable to the size of quantum dots sought and then fabricate the quantum dots by self-assembly of adatoms deposited on the patterned substrate. The severely restricted diffusion field defined by the holes will dominate nucleation and growth to produce a single quantum dot in each etched hole.

At the end of Phase I, we had demonstrated reproducible transfer of the nano-pattern from the biomolecular template into the Si(100) substrate by the LE4 etching process. After LE4, the bio-derived titania etch mask was stripped by dipping the samples in hot sulfuric acid solutions. Attempts to deposit an ordered array of GaAs quantum dots on the nano-patterned and stripped substrate by MBE led to the hypothesis that the nano-patterned surface was in fact oxidized after stripping of the bio-derived etch mast, and that the presence of the oxide over-rode the influence of the etched nano-pattern on formation of the dot array. Accordingly, the central focus of our Phase I Option work has been to develop stripping and cleaning processes that leave the nano-patterned substrate free of oxide in order to enable systematic studies of quantum dot deposition conditions, and their dependence on characteristics of the etched nano-array, in Phase II. A secondary focus has been to scale up the nano-patterning process to cover 1-in diameter substrates, in anticipation of device applications.

2.0. OBJECTIVES

These focus directions were pursued through the following specific objectives:

2.1. to develop a method for removing oxide from the nanopatterned Si(100) substrate after stripping the bio-derived etch mask

Impurities, including surface oxides, influence the adsorption and diffusion of ad-atoms on the nano-patterned substrate, and hence also the nucleation and growth of clusters on that substrate. The substrate must be clean in order to fully expose the effect of the nano-pattern on growth of quantum dot arrays.

2.2. to deposit Ge dots on the nanopatterned Si(100) substrates

Nucleation and growth of dots of an *atomic* solid represent the simplest conceptual study for revealing the effects of the nano-pattern on formation of the dot array. Moreover, arrays of Ge dots on Si(100) have numerous potential applications in quantum effect electronic devices.

2.3. to deposit GaAs dots on the nanopatterned Si(100) substrates

Nucleation and growth of dots of a *compound* solid represent a more challenging conceptual study for revealing the effects of the nano-pattern on formation of the dot array. Moreover, arrays of GaAs dots on Si(100) have numerous potential applications in quantum effect opto-electronic devices.

2.4. to characterize the nanopatterned Si(100) substrates and quantum dot arrays by High Resolution Cross-Sectional Transmission Electron Microscopy (HRXTEM)

Because the diameter of the etched holes and the distances between etched holes on the nano-patterned surfaces are comparable to the diameter of the AFM tips, it is impossible to image the interior of the etched holes. The only method available for determining accurately the depth and the cross-sectional profile of the etched holes is to cleave the nano-patterned substrate and image it with HRXTEM. Moreover, HRXTEM will be required to determine the shape and structure of the quantum dots that grow in the individual etched holes, revealing structure and morphology of the dots.

2.5. to scale up the nano-patterning process to 1-in. diameter substrates

In peparation for device applications, it is necessary to scale up the nano-patterning process from the small 8 mm X 8 mm samples used to date to realistic wafer sizes by showing that the biomolecular template can be applied and the LE4 process carried out uniformly over a wafer. As a first step, we have applied the S-layer biomolecular templates to Si(100) wafers one inch in diameter and etched these by LE4.

3.0. WORK PERFORMED: EXPERIMENTAL PROCEDURES AND RESULTS

3.1. Surface Analysis and Cleaning of the Nano-patterned Substrate After Stripping

A typical small sample (4 mm X 8 mm) that had been etched by LE4 as described in the Phase I Final Report was stripped in hot sulfuric acid. After air exposure and transport to a Group IV MBE system equipped with Auger Electron Spectroscopy (AES), the sample was washed progressively in methanol and acetone, then briefly dipped in dilute HF, blown dry with nitrogen, and loaded into the system. The sample was pumped to a baseline pressure of 2×10^{-9} Torr at room temperature, and examined by AES. The spectrum had peaks only for Si, C, and O. This demonstrated that the stripping process had removed all the titanium from the bio-derived titania etch mask. Successive heating cycles to 850 C showed progressive reduction of the O signal, but less reduction for the C signal. Figure 1 shows the spectrum after cumulative annealing at 850 C for 35 minutes. Subsequent examination of this same sample by AFM showed the etched nano-pattern was still intact on the surface after this annealing program in ultrahigh vacuum.

The surface represented in Figure 1 would in general Group IV MBE practice have too much C to be considered a suitable substrate for deposition. Therefore we sought to remove C more thoroughly on subsequent samples by employing a Piranha etch (sulfuric acid plus hydrogen peroxide) after stripping the mask. Meantime, we had successfully scaled up the nano-patterning process to 1-inch diameter samples, which are more suited for the MBE system than the small samples used earlier to develop the

FIG. 1

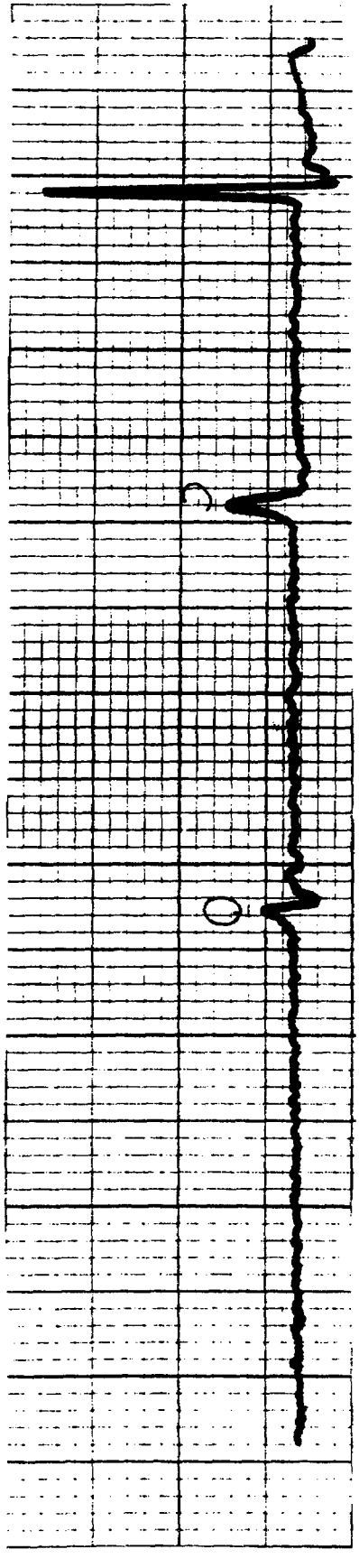
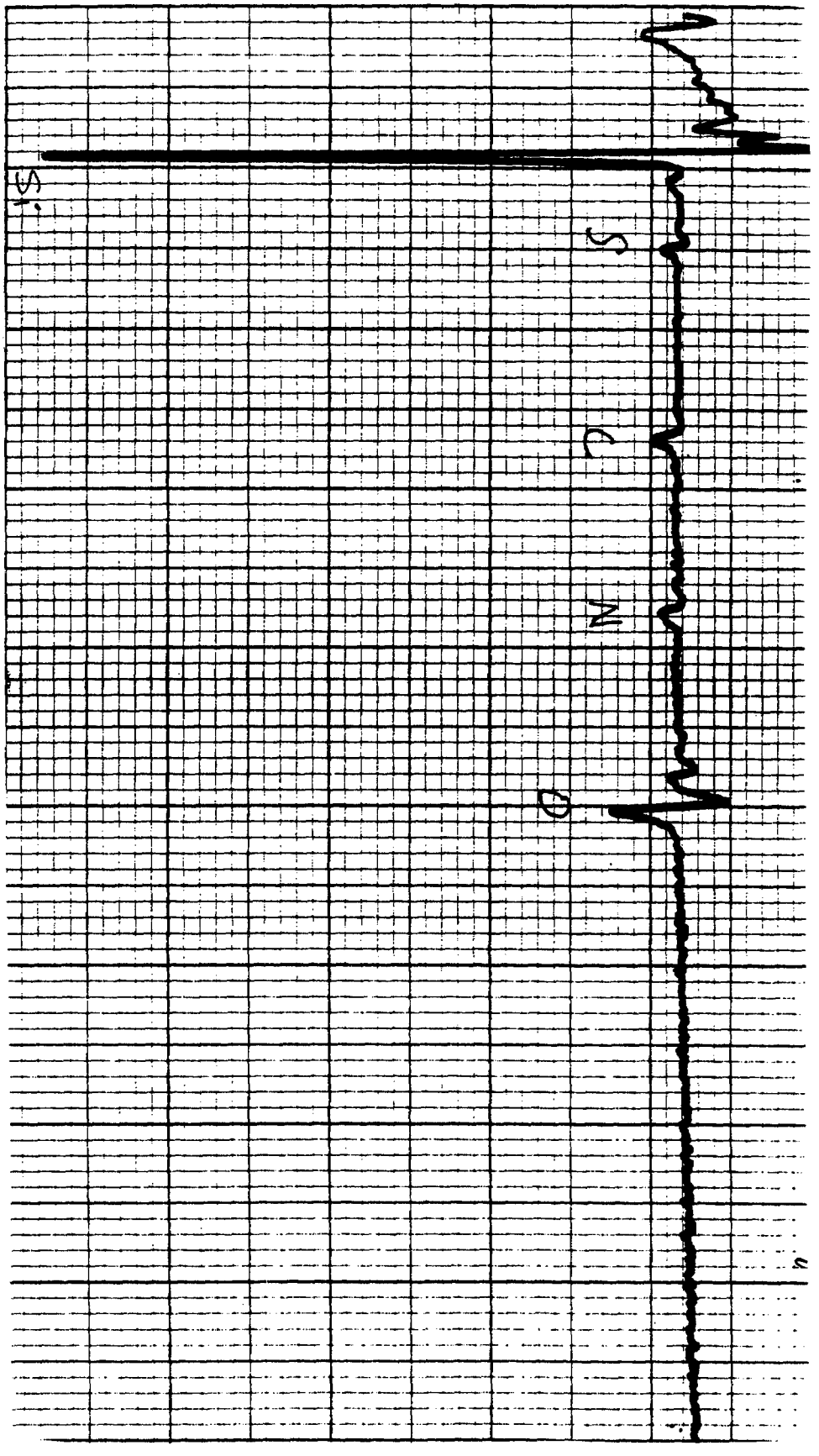


FIG. 2



patterning process. (See below.) Sample #1-1, one inch in diameter, was cleaved into quarters after stripping; one quarter received a 2-minute Piranha etch, and the other received a 25-minute Piranha etch. Afterwards, both were briefly dipped in dilute HF. Figure 2 shows the AES spectrum of the 2-minute Piranha etched sample after it was subsequently annealed in UHV at 850 C for 40 minutes. The Piranha has indeed reduced the C signal relative to that in Figure 1, but at the cost of introducing small signals from S and N

We hypothesized that the C and N were decomposition products of the S-layer biomolecular template that were left on the surface when the titania mask was stripped in hot sulfuric acid. Therefore, we performed an experiment to determine whether piranha cleaning (70% H_2SO_4, 30% H_2O_2), which is a standard method for removing C from Si wafers in preparation for fabrication of integrated circuits, could be used to remove the carbon from our nano-patterned substrates. The risk here is that the piranha treatment is a highly oxidizing solution, and may therefore completely oxidize the nano-pattern on our substrates. If this happens, the subsequent cleaning steps to remove the oxide would remove the nano-pattern. The need to preserve the nano-pattern and the need to remove the C require that a compromise be found.

We conducted experiments to determine how long our nano-patterned samples could be exposed to piranha cleaning, and still have an intact nanopattern (after subsequent removal of oxide by dipping in dilute HF solution). To determine this cleaning time, we cleaved a nano-patterned, sulfuric acid-stripped sample into several smaller pieces. We then placed these pieces in a piranha solution and removed then one at a time at one-minute intervals. Ten minutes was the longest time a sample soaked in the piranha solution. All the samples were rinsed with distilled water and blown dry with nitrogen. We then dipped the samples in a 10% HF solution to remove the oxide, and examined the samples with AFM. We determined that piranha treatments longer than 2 minutes oxidized the pattern completely, resulting in a flat surface after HF etching. Therefore, piranha cleaning of our nano-patterned substrates must be shorter than 2 minutes in duration.

Our next step is to perform AES measurements on samples that have been exposed to a 2-minute piranha etch to determine whether this treatment removes residual C left on the nano-patterned substrates after stripping the biomolecular-generated etch mask, and whether ordered arrays of quantum dots can be grown on such piranha-cleaned nano-patterned substrates.

Progress on these measurements has been held up by extended down-time for the Group IV MBE system (equipped with AES capabilities) to which we have arranged access for these studies. Interruption of the power to the laboratory caused this ultrahigh vacuum system to be precipitously vented to atmospheric pressure during operation, with consequent damage to all hot filaments and evaporation sources. We are participating in the restoration of this system, and also moving rapidly to assemble from our own resources a rudimentary version of the system adequate for continuing these crucial cleaning studies and Ge deposition.

3.2. Ge Dot Deposition on Nanopatterned Si(100) Substrates

Although the surface in Figure 2 still requires further cleaning—through some optimized combination of wet etching and UHV annealing designed to remove the titania

mask and S-layer residues without degrading the etched nanopattern—we chose to attempt Ge dot deposition on this surface. The two quarters of Sample #1-1 prepared as above were simultaneously exposed to Ge from a Knudsen cell at the rate of 0.5 Å·min^{-1} to deliver a total dose equivalent to 10 monolayers. The sample temperature was held at 650 C during deposition.

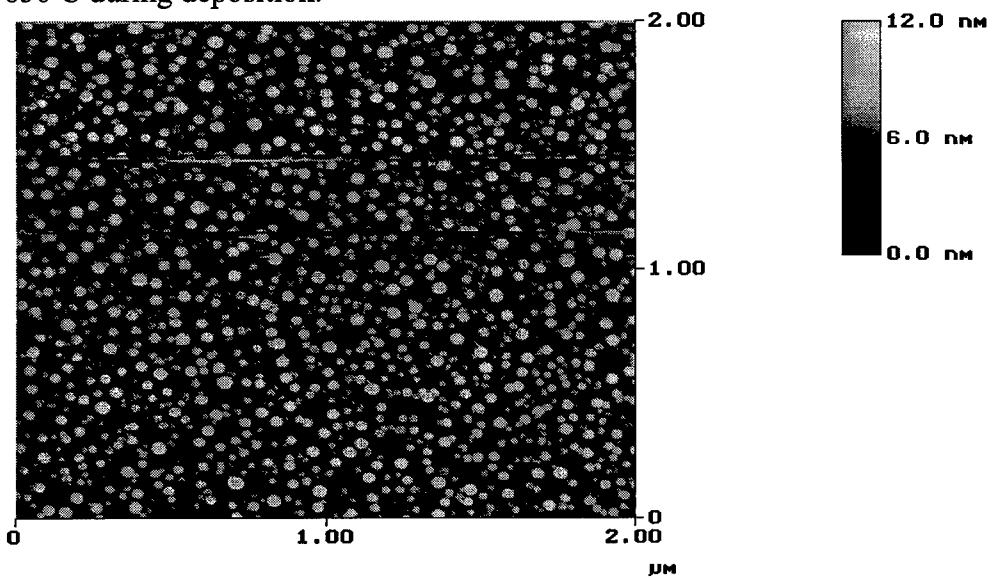


Figure 3A. Deposition of Ge on sample treated with 2-minute Piranha etch after stripping the titania mask.

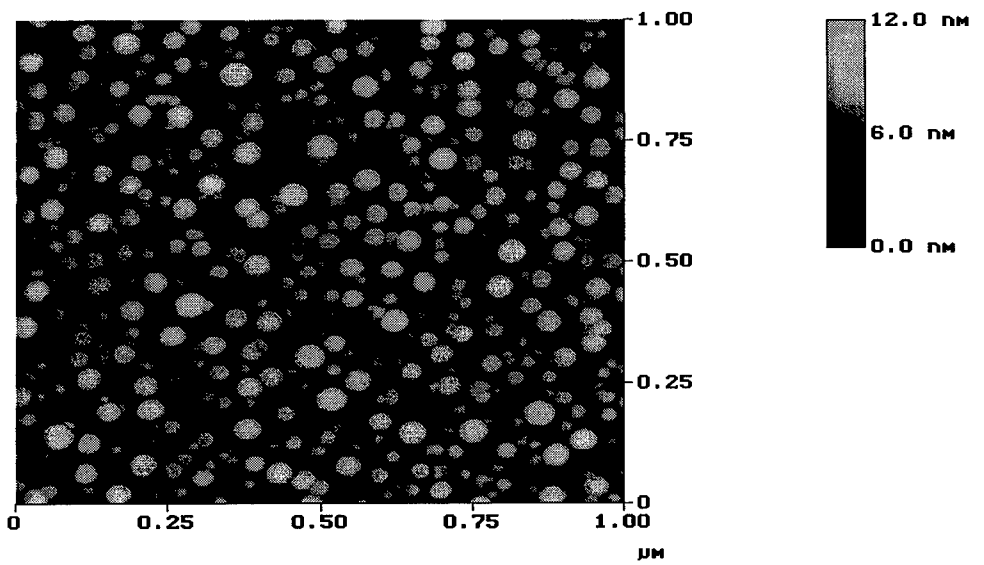


Figure 3B. Deposition of Ge on sample treated with 2-minute Piranha etch after stripping the titania mask.

Both quarter-wafer pieces showed formation of dots after Ge deposition, but neither had the hexagonal symmetry of the nano-array of holes etched onto the substrate. The quarter treated with 2-minute Piranha (Figure 3A, Fibure 3B) showed larger dots than the quarter treated with 25-minute Piranha (Figure 3C). It was later determined by AFM that the etched nano-pattern had been removed during the 25-minute Piranha treatment, and that the surface was essentially flat.

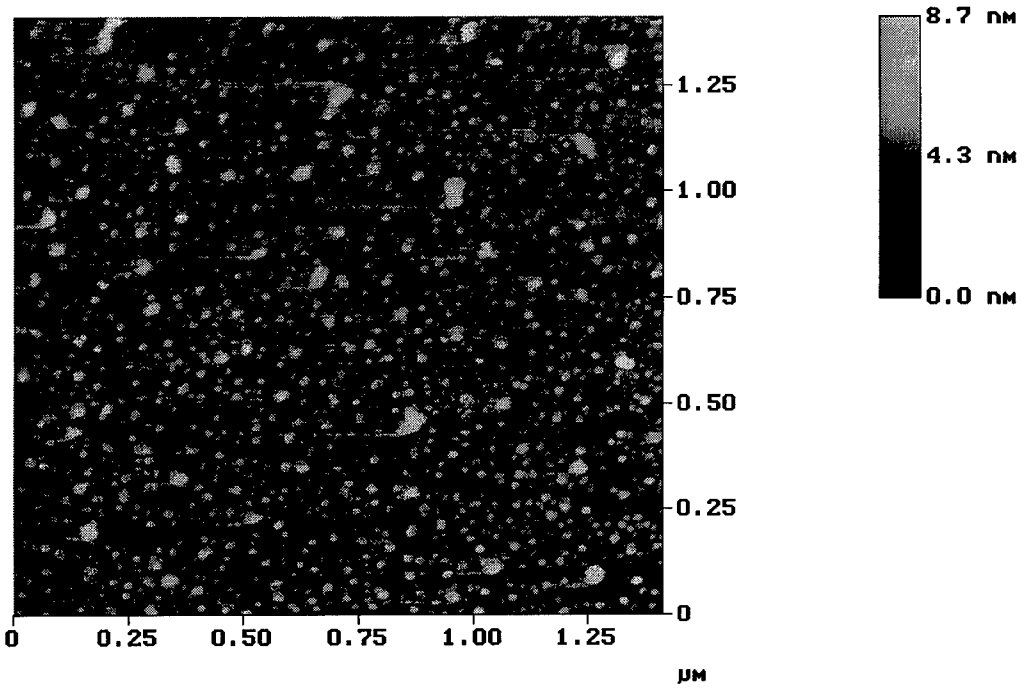


Figure 3C. Deposition of Ge on sample treated with 25-minute Piranha etch after stripping the titania mask.

This very crude first attempt to deposit Ge dots shows at the least different results for a nearly flat substrate and for a substrate on which the etched nano-pattern is intact. Systematic work is required to elucidate the relation between surface cleanliness of the nano-patterned substrate, depth of the etched nano-holes, and dose of deposited ad-atoms in order to form an ordered array of dots in the etched nano-holes.

3.3. GaAs Dot Deposition on Nano-patterned Si(100) Substrates

Near the end of Phase I, our attempts to grow arrays of GaAs quantum dots on our nano-patterned Si(100) substrates produced results indistinguishable from the results on a non-patterned, flat Si(100) wafer. This was our first hint that our nano-patterned substrates were oxidized after stripping the mask, and led us to start the studies of surface cleaning described in the previous section. Having made progress toward cleaning the nano-patterned substrates (but not yet having completely solved the problem) we attempted once again to grow arrays of GaAs quantum dots on our nano-patterned surfaces, but first using the results from the previous section to clean the nano-patterned substrates.

Pieces of two 1-in diameter nano-patterned samples (#1-1 and #1-4) that had been stripped in sulfuric acid and demonstrated by AFM to have the nano-patterned holes in place were subjected to piranha etch less than 2 minutes in length, dipped in 10% HF solution, blown dry in clean nitrogen, and then mounted in the III-V MBE system in the laboratory of Dr. Kris Bertness, NIST-Boulder. This system lacks AES capabilities, but it does have Reflected High Energy Electron Diffraction (RHEED) capabilities that can monitor the symmetry of each layer added to a substrate during epitaxial growth. Although RHEED does not provide compositional information about the surface, the structural images obtained do suggest whether the surface is covered with oxide. The samples as loaded showed no RHEED pattern, suggesting random coverage of oxide on

the surface. The samples were heated to 500 C for 30-60 minutes, after which a faint RHEED pattern was obtained, in which the position of the diffraction spots showed some alignment to the crystalline axes of the sample. This indicates at least partial removal of the oxide. One of the two samples was then heated to 800 C for 10 minutes, and the other to 850 C for 5 minutes. The RHEED patterns showed no further improvement after the high-temperature treatment.

These two samples were exposed to GaAs growth as follows. Each run started with a 2s pulse of As to the sample, followed by six growth cycles alternating between Ga and As, with the Ga coverage about 1 ML per pulse. The samples were held at 450 C during growth, then cooled to 250 C in a flux of As.

The RHEED pattern showed interesting changes after 2-3 monolayers of GaAs deposition. The pattern showed distinct bright spots with a strong hexagonal symmetry, aligned with the crystal axes of the Si(100) substrate. By contrast, the RHEED patterns in our first attempts to deposit GaAs late in Phase I (see above) showed no discernible change upon exposure. Clearly the surface cleaning procedures we have used (brief piranha etch followed by HF dip and thermal desorption in ultrahigh vacuum) have influenced the deposition process at the nano-patterned substrates.

These samples were examined by AFM after GaAs deposition. The results for the sample that was heated to 850 C for 5 minutes in preparation for growth are shown in Figures 4 – 8, which are presented in increasingly higher magnification . In the lower magnification images, regions with the general shapes of S-layer patches are readily visible, in which the density of dots appears to be lower than the density in the areas between these regions. Fourier transforms of the AFM images inside these shaped regions are not those characteristic of a random, unordered surface. Although we cannot demonstrate conclusively that these shaped regions were in fact once covered with S-layer patches, and are therefore regions that had the nano-pattern before GaAs deposition began, is is plausible that these are indeed nano-patterned regions, in which the arrangement of GaAs dots is quite different than on the nearby flat surfaces. The highest magnification shows that the dots are < 40 nm in diameter. A series of images of the sample that was heated to 800 C for 10 minutes showed that GaAs dot formation was much less apparent on this surface, and the Fourier transforms were much more typical of unordered surfaces. On the highest magnification images of that series is shown here, in Figure 9.

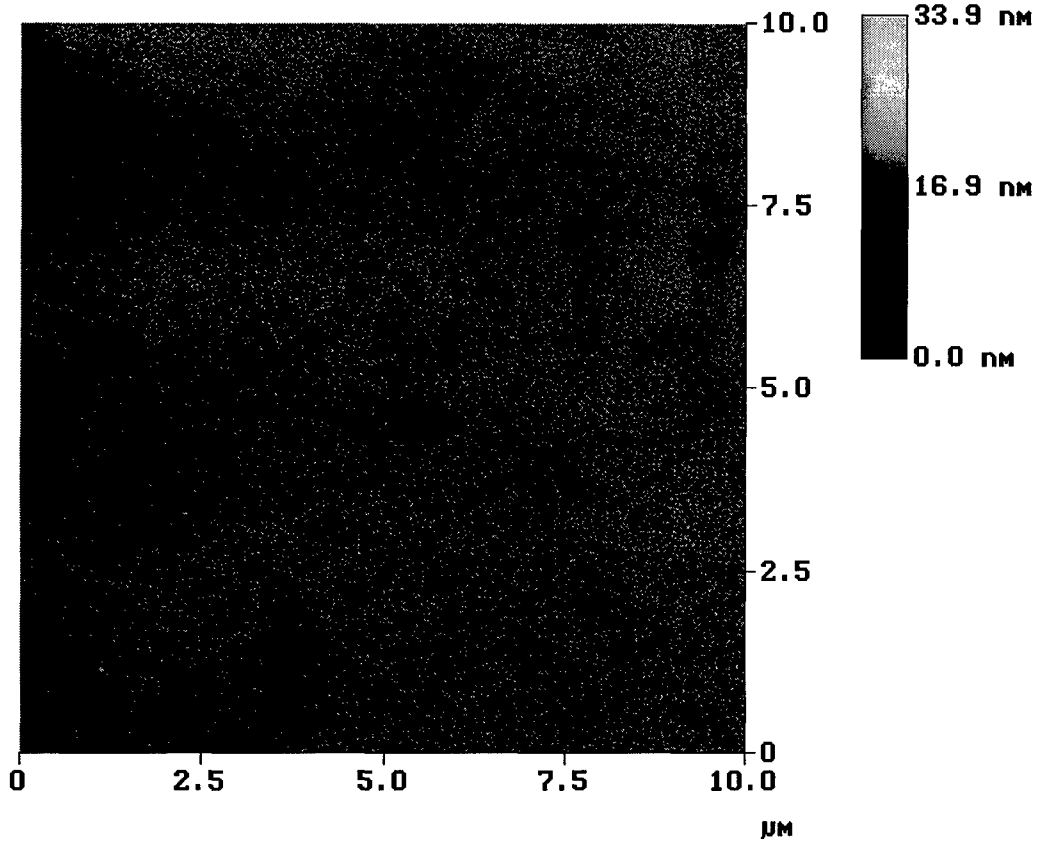


Figure 4. Higher temperature sampled imaged at low magnification.

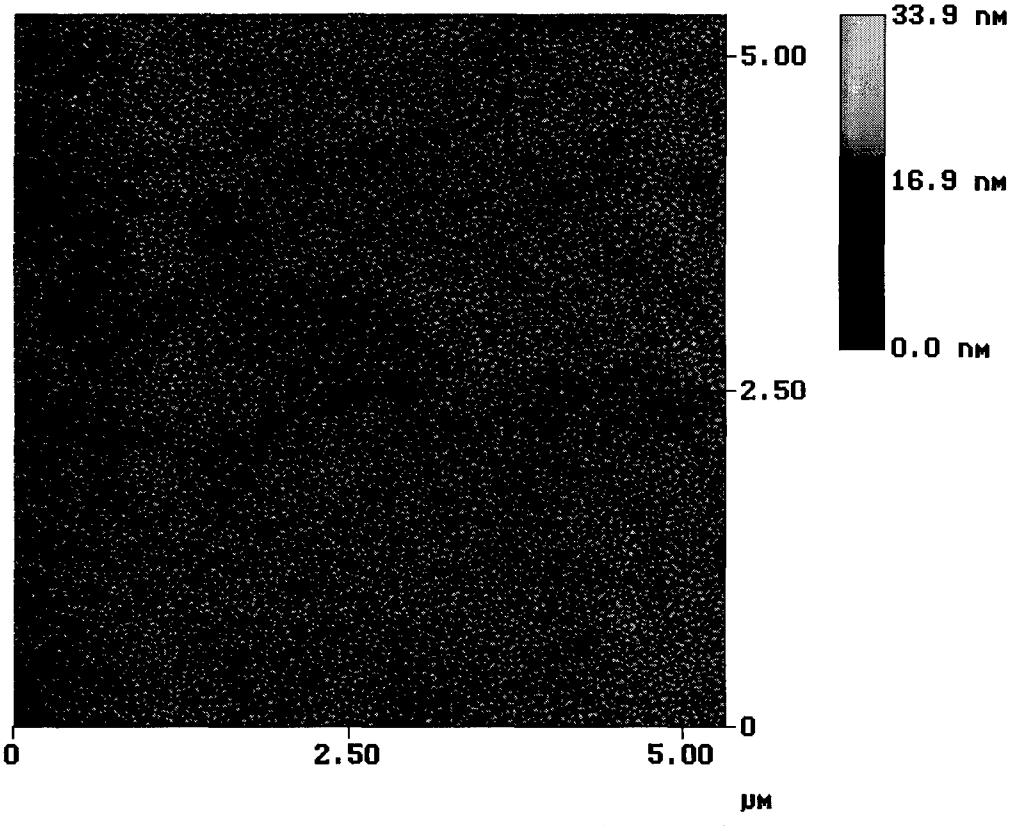


Figure 5. Higher temperature sample imaged at higher magnification.

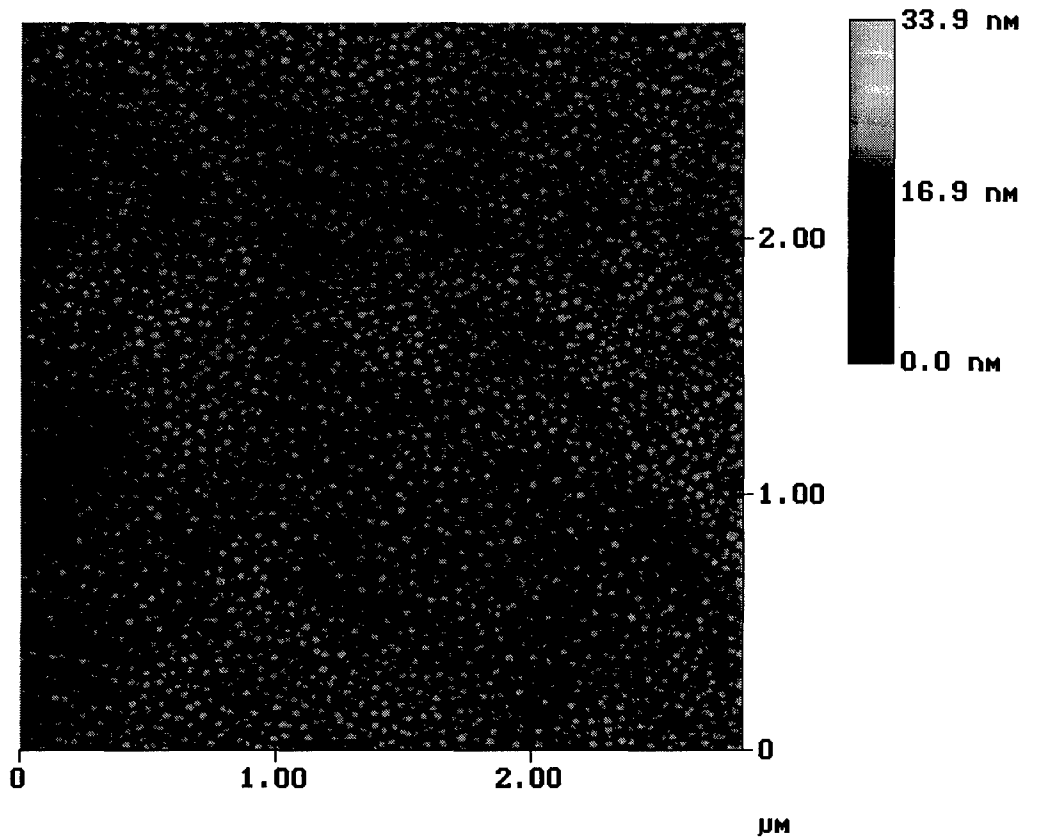


Figure 6. Higher temperature sample imaged at medium magnification .

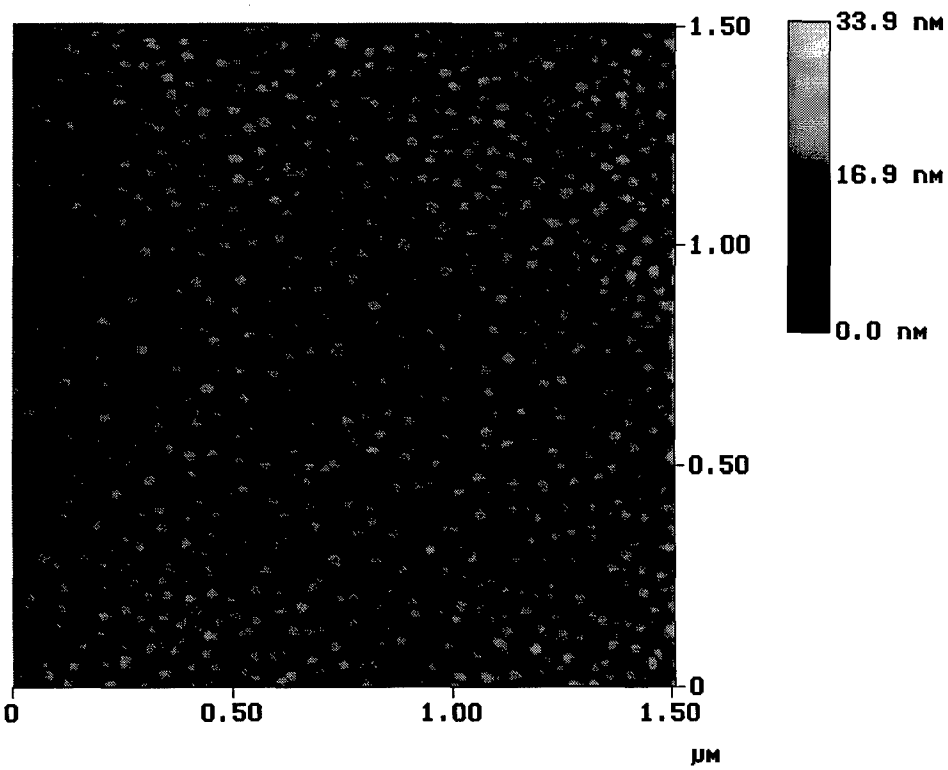


Figure 7. Higher temperature sample imaged at high magnification.

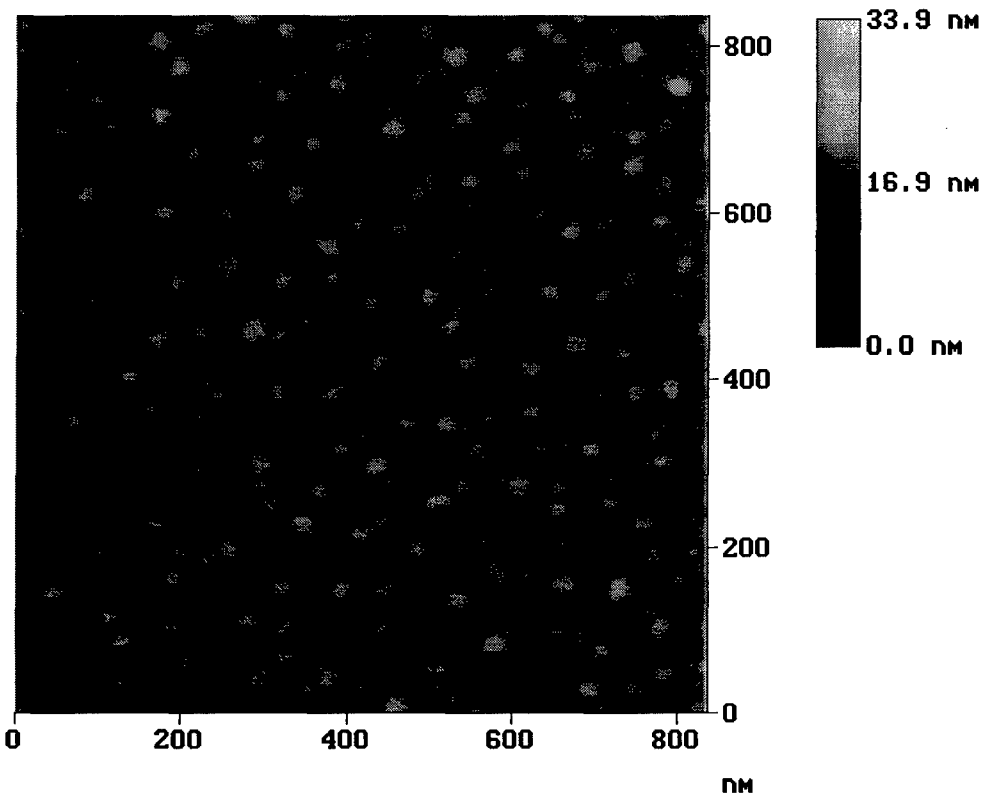


Figure 8. Higher temperature sample imaged at quite high magnification.

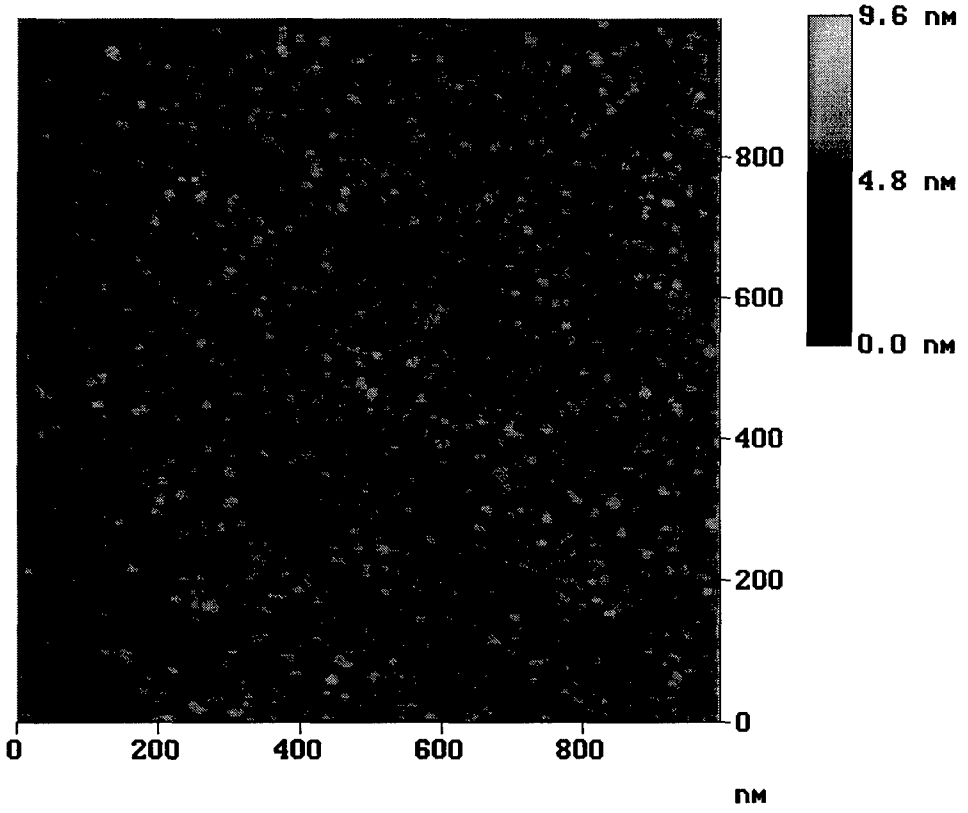


Figure 9. Lower temperature sample imaged at quite high magnification.

Clearly the combination of a brief piranha etch followed by thermal desorption in ultrahigh vacuum at 850 C has improved the dot deposition process on our nano-patterned substrates, but it still has not led to dot arrays which reflect the symmetry of the underlying nano-pattern. This is at least partly due to the fact that at present we are not certain that our combined prianha-desorption method has thoroughly cleaned the surface of O and C, since RHEED provides no direct information on composition of the surface. It is necessary to complete the systematic cleaning study described in the first section of this report. AES studies must be carried out on nano-patterned substrates after a 2-minute piranha etch in order to confirm that the piranha did indeed remove the C, and to determine the temperature and the holding time at that temperature required to desorb the O in ultrahigh vacuum. Of course these experiments must be cross-checked with AFM to confirm that the nano-pattern is not destroyed in the thermal desorption process.

When complete, these studies will allow specification of a standard post-stripping cleaning process that can be applied to our nano-patterned samples just before they are used for MBE depositon of Group IV quantum dots or of Group III-V quantum dots. Clearly, this standardized cleaning recipe is essential to enable determination of the range of growth parameters (sample temperature, ad-atom flux) required to achieve nucleation and growth of one quantum dot in each hole etched in the nano-patterned substrate.

3.4. HRXTEM Analysis of Nano-patterned Substrates

Because the diameter of the etched holes and the distances between etched holes on the nano-patterned surfaces are comparable to the diameter of the AFM tips, it is impossible to image the interior of the etched holes. The only method available for determining accurately the depth and the cross-sectional profile of the etched holes is to cleave the nano-patterned substrate and image it with HRXTEM. Moreover, HRXTEM will be required to determine the shape and structure of the quantum dots that grow in the individual etched holes, revealing structure and morphology of the dots. The quality of the dots will be strongly affected by the microstructure of their interfaces with the etched holes. This atomic-scale structure can be revealed by detailed analysis of image contrast at the interfaces which can identify the position and height of interfacial steps. This is the key technique for evaluating abruptness and smoothness of the crucial interface.

For all these reasons we have introduced HRXTEM into the project at the present point, to prepare for its key role in the dot/hole interfacial studies in our Phase II project. This analysis will be provided by the laboratory of Prof. Z.L. Wang in the Department of Materials Science and Engineering at Georgia Tech. To demonstrate the quality of the HRXTEM images that will be available to our project, we show in Figure 10 an image of one of our substrates (without the nano-pattern in place) which as been exposed to a Ge dose comparable to that we used in our attempts to deposit Ge dot arrays described in the first section of this report. The abruptness of the interface and the atomic resolution of the interfacial region, demonstrated by the lattice lines, is readily apparent. Comparable images of the interfacial region between our quantum dots and the etched holes in which they grow will play a crucial role in optimizing the conditions needed to achieve one dot in each hole, and in elucidating the influence of that interface on the structural properties of the quantum dots themselves.

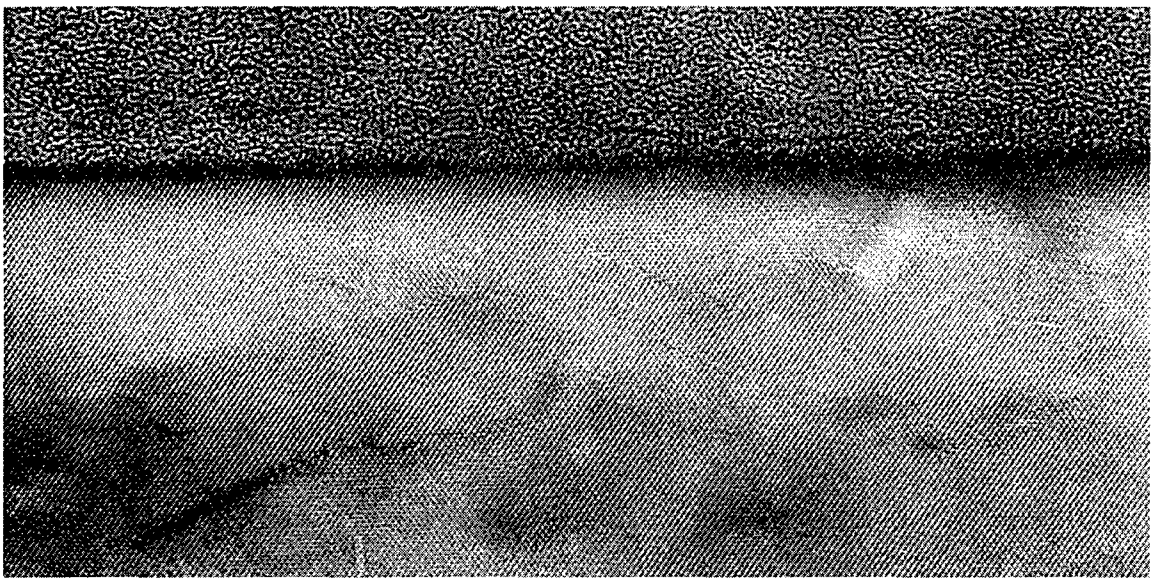


Figure 10. HRXTEM image of Ge deposited on Si(100).

3.5. Nano-pattern Formation on 1-inch Si(100) Substrates

In peparation for device applications, it is necessary to scale up the nano-patterning process from the small 8 mm X 8 mm samples used to date to realistic wafer sizes. As a first step, we have applied the S-layer biomolecular templates to Si(100) wafers one inch in diameter and etched these by LE4. Our AFM capabilities will not scan full wafers, so selected areas from different regions of the wafer must be scanned and compared. Figures 11A and 11B show one such region, at two levels of magnification, from Sample 1-1. This sample had been stripped in hot sulfuric acid, dipped in 10% HF, and flashed with 12 Angstroms of titanium. These results are typical of those seen across the wafer, all of which together demonstrate that the nano-pattern was etched uniformly across the wafer, despite the fact that the pattern is not spatially coherent over that distance. Regions such as these, with subsequent Piranha etches and UHV annealing, were used for the Ge dot deposition shown in Figure 3ABC.

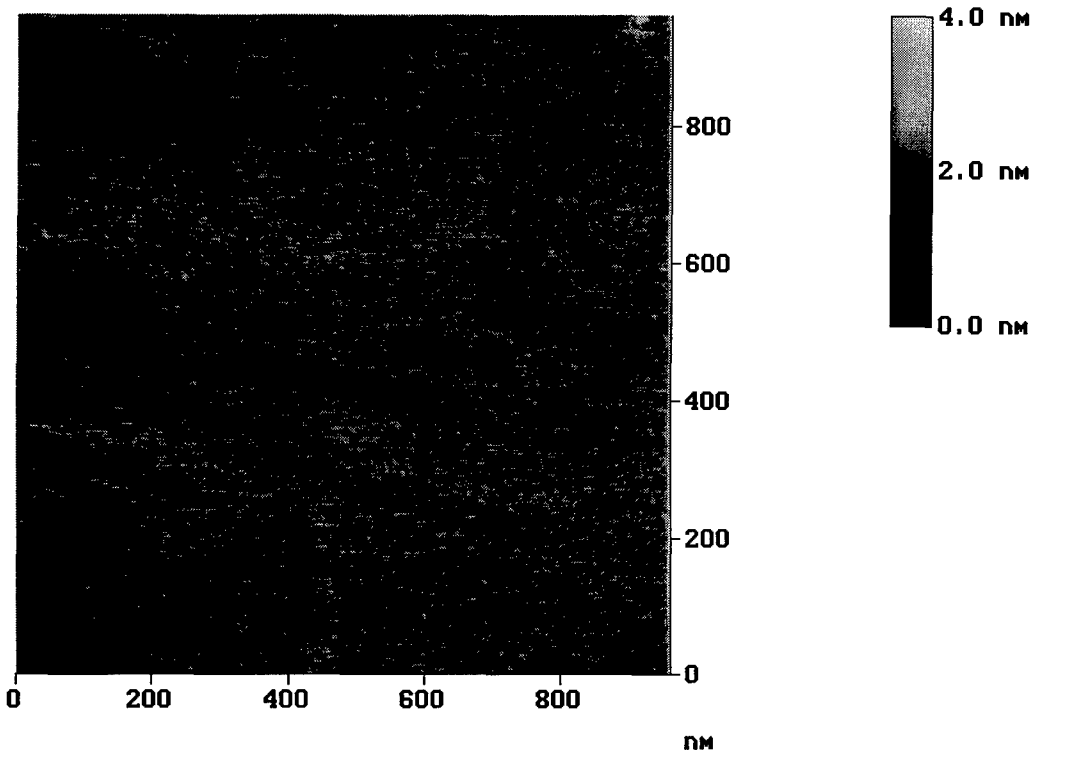


Figure 11A. Selected region from Sample 1-1 after stripping.

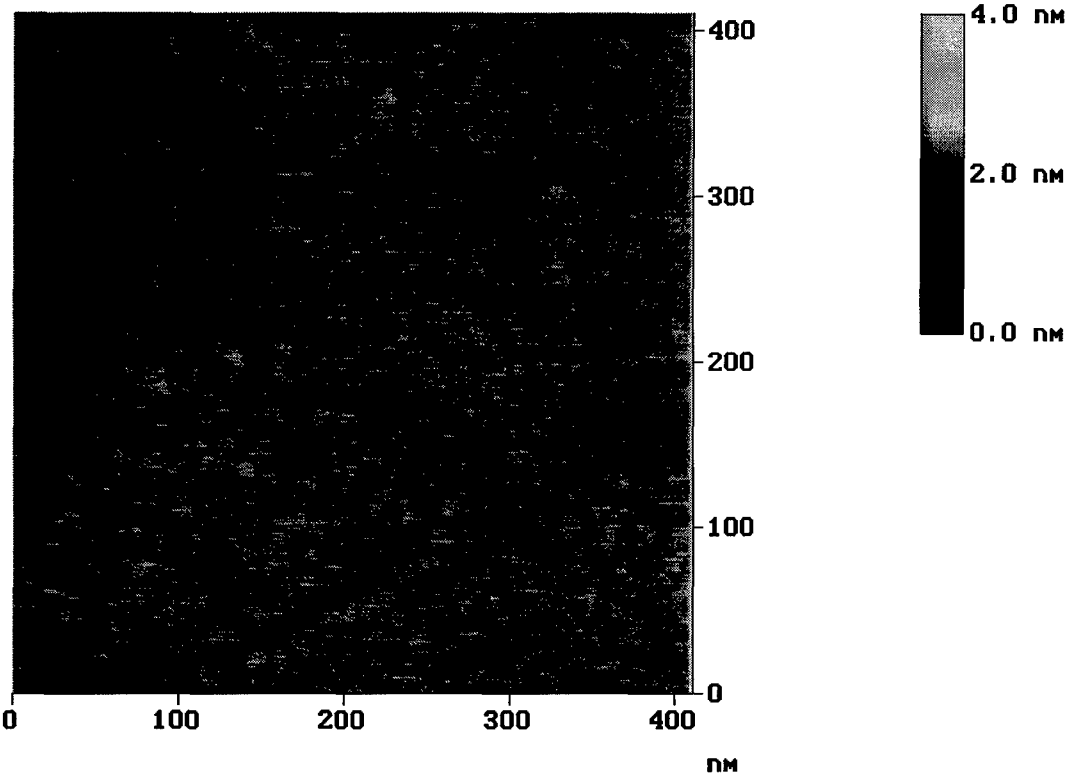


Figure 11B. Same region as in Figure 11A, with higher magnification.

Another 1-in diameter sample, Sample #1-4, was etched by LE4 using slightly smaller electron current density to the sample. The result is noticeably better definition

and uniformity in the nano-hole patterns. Again, etching was uniform across the sample, and typical images are presented in Figures 12A-12C.

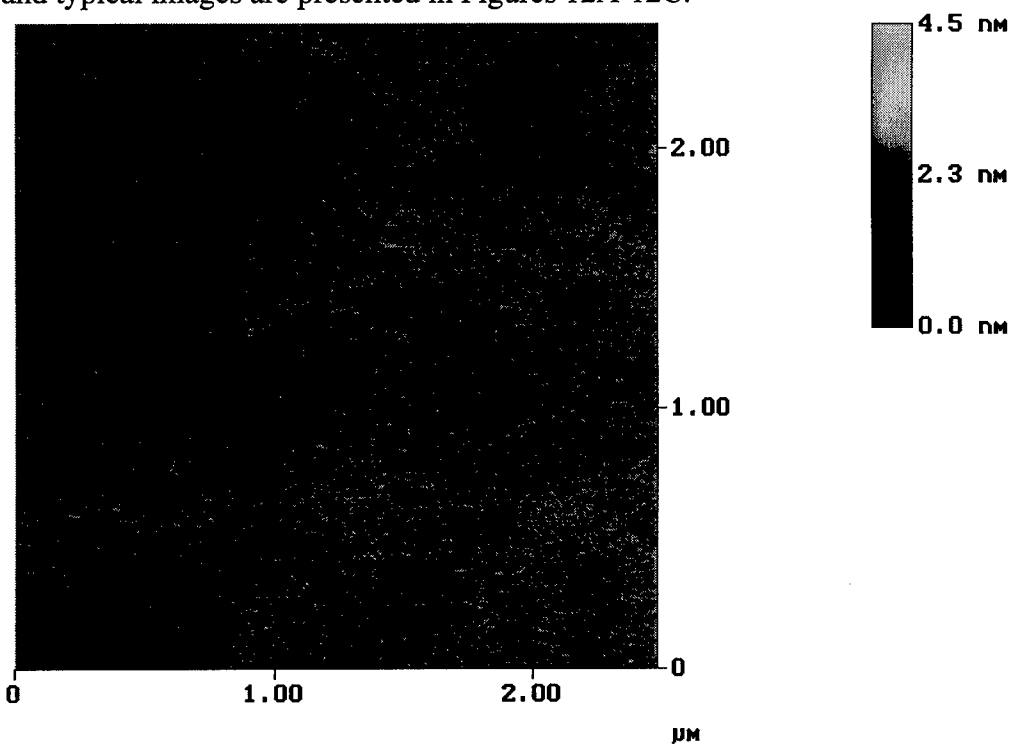


Figure 12A. Low magnification scan of region from Sample 1-4, showing several contiguous zones of nano-holes, each zone defined by a single S-layer patch during LE4.

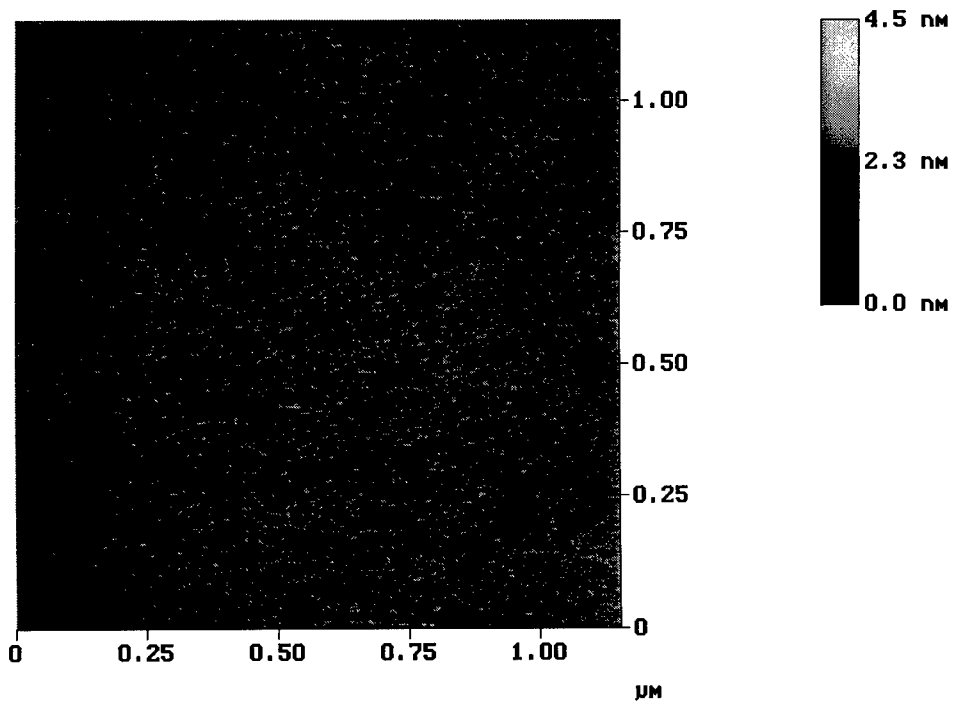


Figure 12B. Higher magnification scan of region from Sample 1-4, showing detail of the zone of nano-holes defined by a single S-layer patch during LE4.

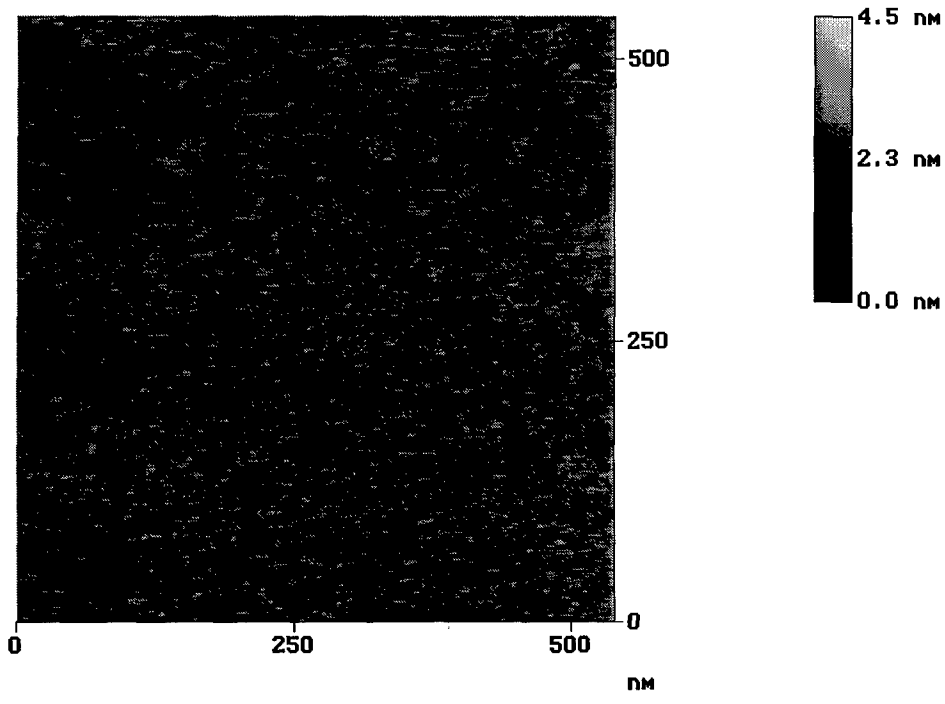


Figure 12C. Still higher magnification scan of region from Sample 1-4, showing close-up detail of the nano-hole array defined by a single S-layer patch during LE4.

Patterned Si(100) substrates such as those shown in Figure 12ABC can now be produced routinely, and in sizes (1-in diameter wafers) convenient for subsequent growth studies by MBE.

4.0. DISCUSSION AND FEASIBILITY OF THE APPROACH

Our approach to forming ordered arrays of semiconductor quantum dots on a substrate relies on five key steps:

- Attach S-layer templates to a clean, hydrophobic Si(100) substrate and convert them to a titania etch mask;
- Transfer the pattern into the substrate using LE4;
- Strip the titania mask from the sample after LE4, and confirm that the nano-array has been defined in the substrate;
- Remove oxide and other impurities from the nano-patterned substrate after stripping the mask;
- Grow one semiconductor quantum dot in each hole of the array to form an ordered array of quantum dots.

The results achieved in Phase I of this project demonstrate that we have reliable methods for attaching the S-layer biomolecular templates to the Si(100) substrate and converting them into a robust etch mask. We also have reliable methods for transferring this pattern into the substrate by LE4 in the anodic configuration, using 50-50 mixtures of argon and hydrogen. Developing this anodic LE4 process for the nano-pattern was in fact the

central effort in Phase I. We also have a method for stripping the mask, and we can confirm that the nano-array is in place after stripping.

During Phase I Option we demonstrated that the nano-patterned Si substrate was indeed oxidized after the stripping step. We developed a combination of wet etching methods and thermal desorption in ultrahigh vacuum for cleaning the nano-patterned substrate for subsequent quantum dot deposition, and demonstrated via Auger Electron Spectroscopy that our cleaning methods were decreasing the amount of surface oxide. Failure of the ultrahigh vacuum system prevented taking this study to completion and demonstrating total removal of oxide. Nonetheless, we made our first attempts to deposit Ge and GaAs dots even before a definitive cleaning process had been developed. We saw that a nano-patterned surface—despite the presence of residual O, C, and N—displayed arrangements of dots different from those on a flat Si(100) surface but did not yet display the symmetry and dimensions of the underlying nano-pattern. We also scaled up the nano-patterning and stripping process to cover 1-in diameter Si(100) substrates.

We are confident that with restoration of the UHV system our combined cleaning process will remove all oxide and other impurities from the nano-patterned substrate, to enable systematic studies of quantum dot deposition conditions, and their dependence on characteristics of the etched nano-array, in Phase II.

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13. ABSTRACT (Maximum 200 words)

Report developed under SBIR contract for Topic A98-028: The objective is to demonstrate the feasibility of forming precisely ordered and precisely located arrays of semiconductor quantum dots by using biomolecular templates and Low Energy Electron Enhanced Etching (LE4) to define in a substrate an array of holes with diameters comparable to the size of quantum dots sought, and then growing one quantum dot in each "nanohole" by self-assembly of deposited adatoms. In Phase I, keymethodology was developed: (1) depositing the biomolecular templates on clean(hydrophobic) Si(100) surfaces; (2) identifying LE4 process conditions for etching the nano-pattern; (3) stripping the template-generated masks after LE4 by wet chemical methods. Phase I Option emphasized: (1) removal of the oxide left on the nano-patterned substrate by the stripping process; (2) preliminary efforts to deposit Ge and GaAs quantum dots; (3) scaling the nano-patterning and deposition processes to cover 1-in. diameter substrates. These quantum dot arrays have potential applications in optical emitters and detectors, single electron transistors, and high-density memory arrays.

14. SUBJECT TERMS
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16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL